Supplementary Material: Ionene-based physical hydrogels: probing the solution-gel transition, chain and counterion dynamics by means of NMR

Sarrah Mezdari[1], Lingsam Tea[1], Juliette Sirieix-Plénet[1],
François Ribot[2], and Natalie Malikova[1,*]

[1] *Sorbonne Université, CNRS, Laboratory of Physical Chemistry of Electrolytes and Interfacial Nanosystems (PHENIX), 4 place Jussieu, F-75005 Paris, France and*

[2] *Sorbonne Université, CNRS, Laboratoire de la Chimie de la Matière Condensée de Paris (LCMCP), 4 place Jussieu, F-75005 Paris, France*

(Dated: October 19, 2025)

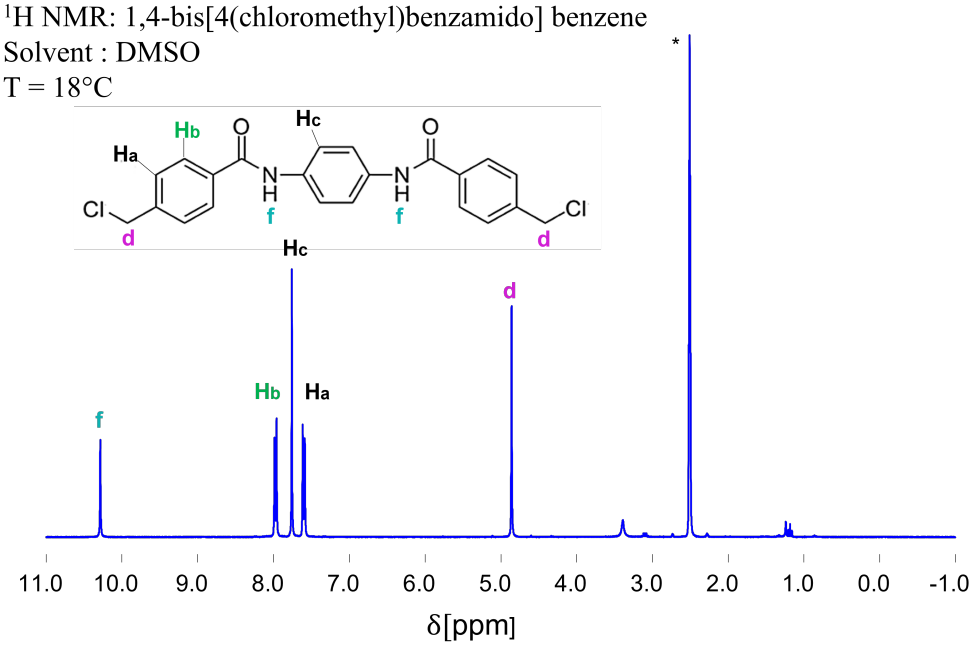

Figure 1: ^{1}H NMR spectra of 1,4-bis[4(chloromethyl)benzamido] benzene. The solvent (DMSO-d6) peak is marked by an asterisk.

---

[1] Y. Misawa, N. Koumura, H. Matsumoto, N. Tamaoki and M. Yoshida, *Macromolecules*, 2008, **41**, 8841–8846

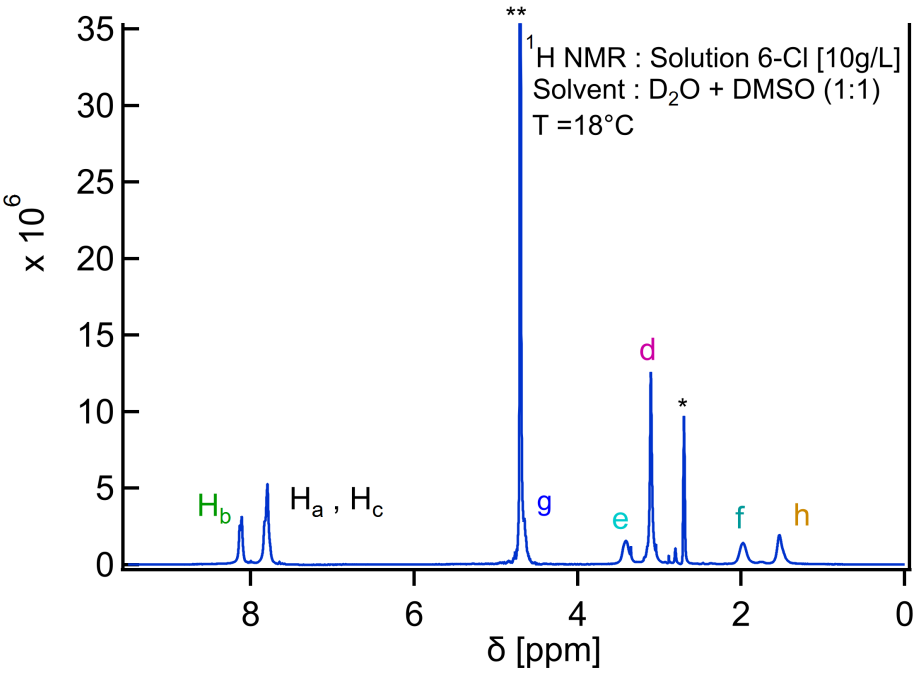

Figure 2: ^{1}H NMR spectra of a 6-Cl modified ionene (Mw = 78 kDa[1]) in DMSO-d6/D2O = 1/1 (v/v) at 9g/L (solution state) . Solvent peaks: * DMSO-d6 and ** HOD. Spectrum is consistent with Misawa et al data [1].

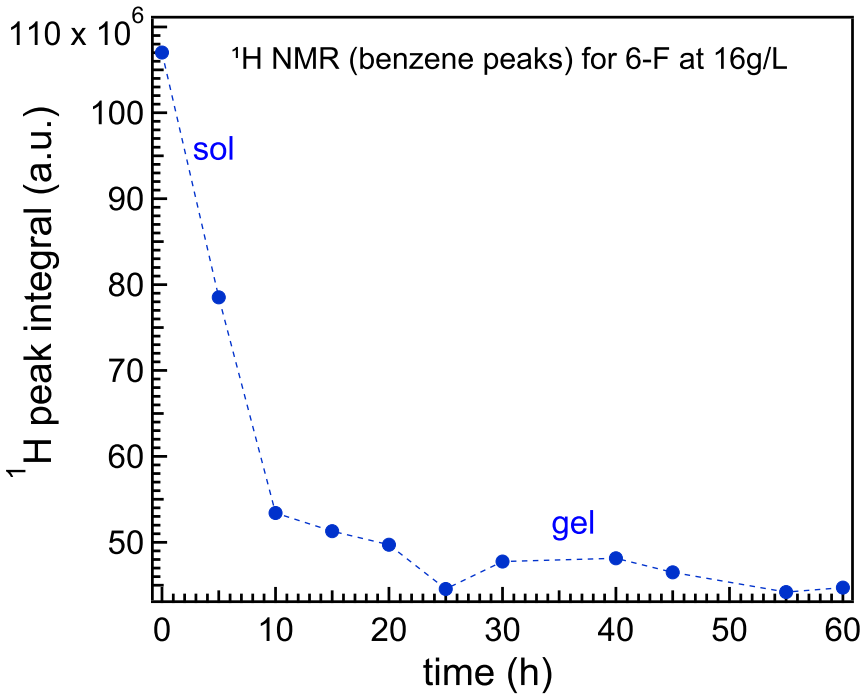

Figure 3: Integrated intensity of the benzene peaks in the ^{1}H NMR spectra of 6-F ionene (16g/L, CGC) as a function of time, showing signal loss as gelation takes place. The temperature for the first point is above room temperature (70°C), the remaining points correspond to 18°C.

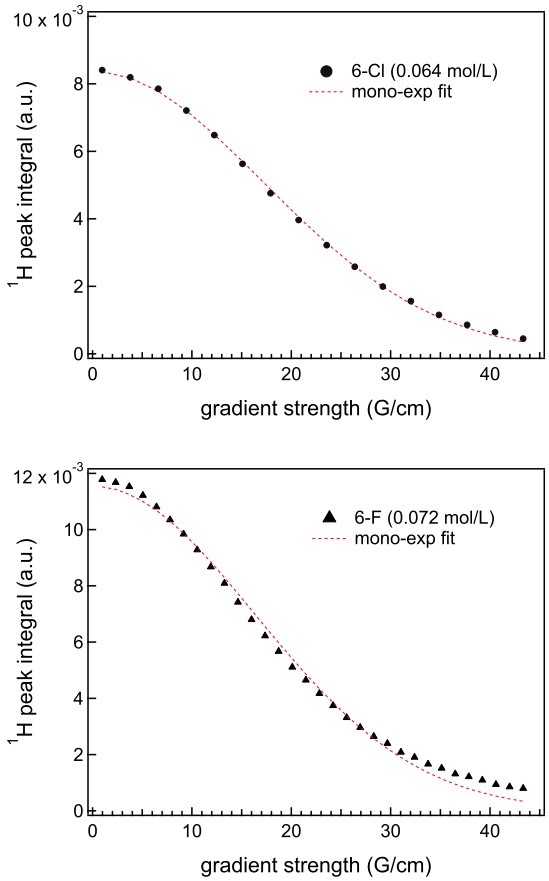

Figure 4: ^{1}H intensity signal attenuation versus gradients strength for peaks at 7-8 ppm (aromatic protons) for (top) 6-Cl gel at 0.064mol/L (38g/L), for which a mono-exponential fit works well, and for (bottom) 6-F gel at 0.072mol/L (40g/L), for which a mono-exponential fit is only approximative. We note that a double exponential would provide a better fit of the decay in Figure 4 (bottom). A double exponential analysis reveals a majority of the chains (70%) moving with a diffusion coefficient D_{fast} = 3.3 x 10^{-11} m^2/s, while 30% of the chains move slower by a factor of cca 3.5 ($D_{slow} = 9.7 \times 10^{-12}$ m^2/s). However, from all information we have on ionene-based hydrogels, we do not see a reason to believe that exactly *two* families of *visible* chains are present in the gel and bi-exponential fitting might be just a misleading approximation of an entire distribution of diffusion coefficients. Thus, in the main text of the article we remain at the mono-exponential fitting, which for the data in Figure 4 yields a single average diffusion coefficient of $D = 2.2 \times 10^{-11}$ m^2/s for all the *visible* chains.

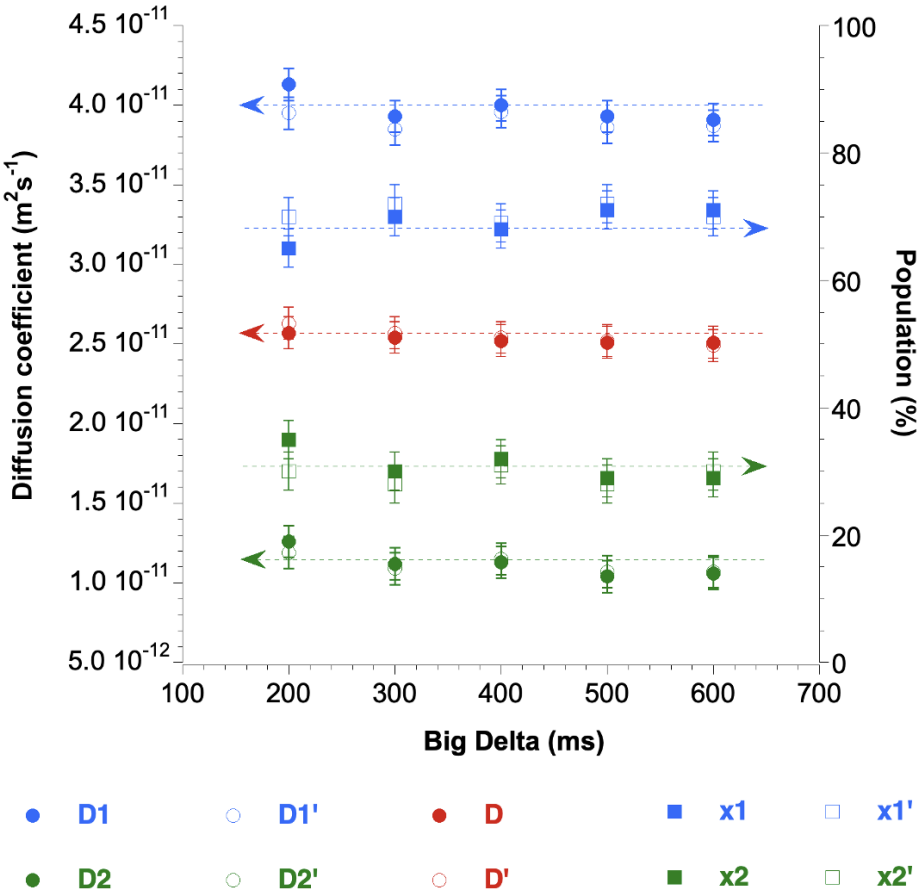

Figure 5: Ionene chain diffusion coefficients and populations in 6-F gel at 0.072mol/L for different diffusion times (Big Delta). The attenuation profiles of the signals around 7.8ppm (H_b) and 7.5ppm (H_a and H_c) have been fitted with the standard Stejskal and Tanner equation using one diffusion coefficient (closed and open red circles) or two diffusion coefficients (fast component: closed and open blue circles; slow component: closed and open green circles). When the analysis was done with two diffusion coefficients, the percentage of each contribution is presented with the same colour code (closed or open squares). Unprimed data correspond to those obtained for the signal at 7.9ppm (H_b) while primed data correspond to those obtained for the signal at 7.5ppm (H_a and H_c). The roughly constant values obtained for diffusion times spanning from 200 to 600ms indicate that any occurrence of two diffusion coefficients cannot be explained by an intermediate exchange between a fast and a slow population.

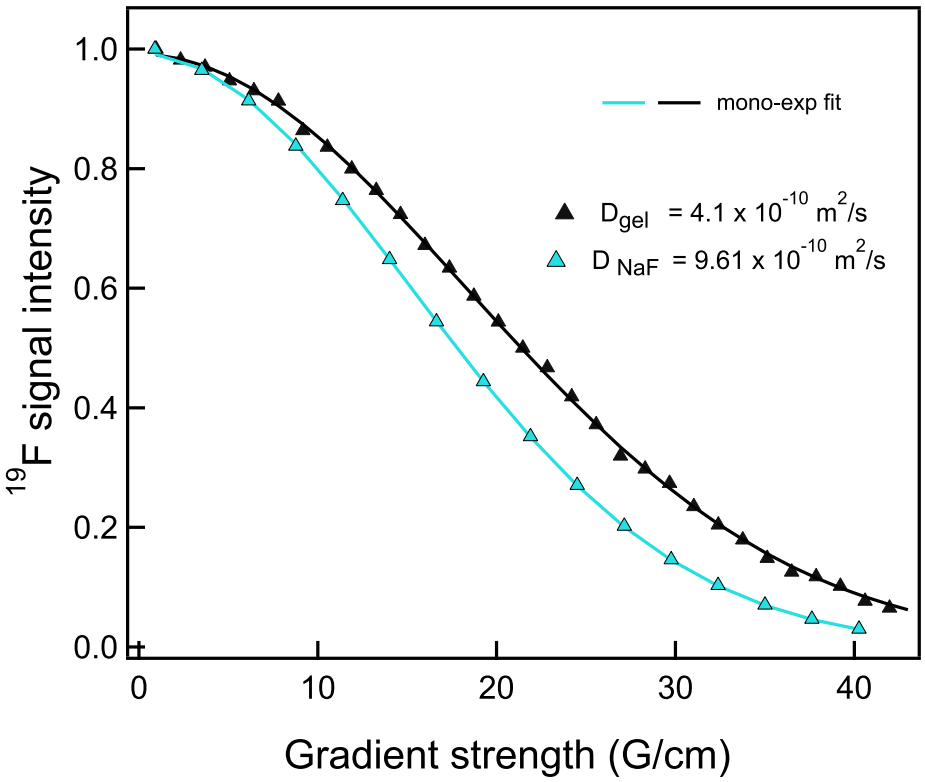

Figure 6: ^{19}F intensity signal attenuation versus gradient strength for fluoride counterions at -122.0 ppm. Measurement done at 18°C.

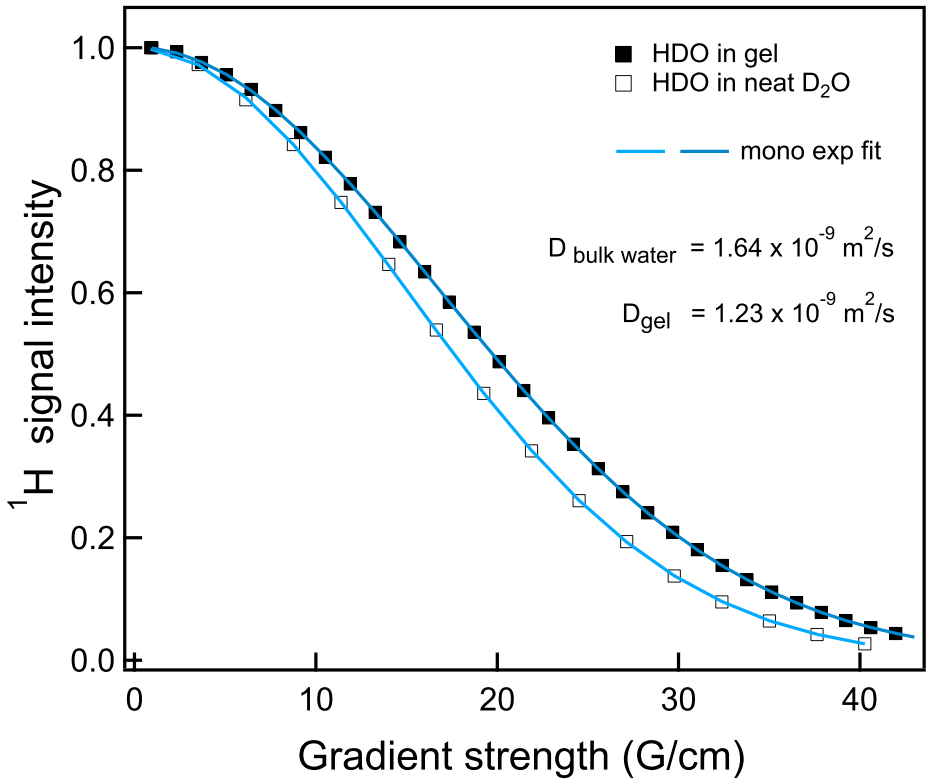

Figure 7: ^{1}H intensity signal attenuation versus gradients strength for water proton peak at 4.7ppm. Measurement done in D_2O at 18°C.